SoilPlusVeg: an integrated air-plant-litter-soil model to predict organic chemical fate and recycling in forests

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ABSTRACT

Current modelling approaches often ignore the dynamics of organic chemicals uptake/release in forest compartments under changing environmental conditions and may fail in accurately predict exposure to chemicals for humans and ecosystems. In order to investigate the influence of such dynamics on predicted concentrations in forest compartments, as well as, on air-leaf-litter fluxes, the SoilPlusVeg model was developed including a forest compartment (root, stem, leaves) in an existing air-litter-soil model. The accuracy of the model was tested simulating leaf concentrations in a broadleaf woods located in Northern Italy and resulted in satisfying model performance. Illustrative simulations highlighted the "dual behaviour" of both leaf and litter compartments. Leaves appeared to behave as "filters" of air contaminants but also as "dispensers", being deposition flux exceeded by volatilization flux in some periods of the day. Similarly, litter seemed to behave as a dynamic compartment which could accumulate and then release contaminants recharging air and vegetation. In just 85 days, litter could lose due to volatilization, diffusion to depth and infiltration processes, from 6% to 90% of chemical amount accumulated over 1 year of exposure, depending on compound physical and

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chemical properties. SoilPlusVeg thus revealed to be a powerful tool to understand and estimate chemical fate and recycling in forested systems.

KEYWORDS: multimedia fate model, plants, litter, PAH, PCB, risk assessment

INTRODUCTION

Vegetation has a fundamental function in controlling air quality (e.g. reducing air concentrations of chemicals and particulate matter, *Terzaghi et al., 2013*) and the accumulation of chemicals in vegetation is the first step in the food chain uptake, influencing both human and environmental exposure and therefore effects. For this reason, vegetation uptake was accounted in current risk assessment modelling tools (e.g. EUSES model, *EC, 2004*) to predict exposure through food. However, it has been underlined the need for more dynamic and ecologically realistic description of vegetation uptake for improving human and ecological risk assessment, given the substantial simplicity of current regulatory approaches (*EC, 2013*). The role of vegetation in accumulating organic contaminants was first studied in the 1980/90s, when different studies were conducted to investigate chemical uptake by plant roots (*Briggs et al., 1982; Briggs et al., 1983; Burken and Schnoor, 1998*) and leaves (*Bacci et al., 1985; Bacci et al., 1990*). Later, the forest filter effect (FFE), i.e. the ability of forest to efficiently sequester chemicals from air and transfer them to the soil, was defined (*McLachlan et al., 1998*) and characterized for different types of forests (*Horstmann and McLachlan, 1998; Jaward et al., 2005; Nizzetto et al., 2006a*). Air-plant exchange was initially regarded as mostly a unidirectional (air $\rightarrow$ plant) flux for atmospheric pollutants; however, a number of studies later demonstrated that leaves behave as a dynamic compartment which, in response to environmental condition changes, can accumulate or re-emit organic contaminants (*Dalla Valle et al., 2005; Gouin et al., 2002; Hornbuckle et al., 1996; Hung et al., 2001*), as well as capture and release particulate matter and its associated chemicals (*Terzaghi et al., 2013*). Litter was also shown to be relevant in the accumulation or release of organic contaminants, influencing concentrations in air and controlling chemical transport across the air-soil interface (*Ghirardello et al., 2010; Liu et al., 2013; Nizzetto et al., 2014*). Over the past two decades, interest in the role of forests in the cycling and fate of persistent organic pollutants (POPs) has increased, as their potential to act as final sink or temporary repository of POPs has been recognized and discussed (*Scheringer and McKone, 2003*).

Also the soil compartment has received much attention in the past twenty years since it was recognized as playing an important role suppling important ecosystem services to humans and environment, e.g., its buffer and filtering function for pollutants allows groundwater and surface water protection (Adhikari and Hartemink, 2016; *Brevik et al.,* 2015; *Keesstra et al.,* 2012; *Keesstra et al., 2016*). More specifically, a number of field studies were conducted to measure organic chemical concentrations in different compartments (air, leaves, litter and soil) of temperate, boreal and tropical forests (*Choi et al., 2008; Jaward et al., 2005; Kompordová et al., 2016; Moeckel et al., 2008; Nizzetto et al., 2006b; Nizzetto et al., 2007; Nizzetto et al., 2008b; Su et al., 2007; Zheng et al., 2015),* while some simplified modeling approaches were developed to estimate chemical fluxes between these compartments *(Moeckel et al., 2009; Nizzetto et al., 2006b; Nizzetto et al., 2007; Nizzetto et al., 2008a).* Recently, the use of a more detailed parameterization of canopy (*Nizzetto and Perlinger, 2012*) and of litter/soil (*Moeckel et al., 2008; Nizzetto et al., 2014*) exchange was suggested, in order to further explore their potential influence on global distribution and fate of organic chemicals. Since the late 1980s, a number of plant bioaccumulation models with different degrees of complexity were developed (*Bathia et al., 2008; Cousins and Mackay, 2001; Czisar et al., 2012; Fantke et al., 2011; Komprda et al., 2009; Legind et al., 2009; Paterson et al., 1991; Priemer and Diamond, 2002; Trapp et al., 1994; Undeman et al., 2009; Wania and McLachlan, 2001; Wegmann et al., 2004).* However, most of these models consider only the variability in exposure concentrations and assume that many plant and environmental parameters are constant over time, lacking ecological realism (*EC, 2013*). Furthermore, they generally furnish a simplified description and parameterization of the air and soil compartments and totally ignore the presence of a litter layer, although its inclusion in multimedia fate models was demonstrated to significantly alter the predictions of organic contaminants between air and soil (*Ghirardello et al., 2010*). The aim of this study was to develop a new dynamic vegetation model that accounts for the variability of meteorological and ecological parameters and integrate it in an existing dynamic air/litter/soil model (SoilPlus) *(Ghirardello et al., 2010).* The final model (SoilPlusVeg) includes two air compartments (Planet Boundary Layer, PBL and residual layer), a

multi-layered litter/soil compartment and a forest compartment (leaves, stem, roots) in which organic contaminants can partition and cycle. A preliminary sensitivity analysis of SoilPlusVeg model was performed and model performance was also evaluated adopting an ecologically realistic and full dynamic scenario developed in previous work *(Terzaghi et al., 2015).* Illustrative simulations were then run in order to show: i) the short-term variability of phenanthrene air-leaf fluxes; ii) the seasonal variability of some Polychlorinated Biphenyls (PCBs) fluxes in a forested system mainly focusing on air-leaf-litter exchanges; iii) the potential of a contaminated litter/soil system to recharge the atmosphere and therefore act as a chemical source for air and vegetation. The results of the present study, dealing with dynamics of air/plant/litter/soil compartment interactions, could be relevant when evaluating the exposure of humans and ecosystems to organic chemicals.

MATERIALS AND METHODS

2.1 Development of the vegetation model and integration with SoilPlus. A new dynamic vegetation model, based on the fugacity approach *(Mackay et al., 2001),* was developed to simulate a forest of trees composed of root, stem and leaf compartments. In this model, compartment capacities are expressed in terms of Z values (**Table A.1**) while transport and transformation processes are computed by means of D values (**Table A.8**). Organic chemicals can reach the vegetation compartments through dry gaseous deposition (absorption), dry particle deposition, rain dissolution of dissolved chemical, wet particle deposition and root uptake from soil; loss processes include volatilization, wash off, wax erosion, litter fall, degradation and transfer from roots to soil; moreover, translocation through xylem and phloem allows the chemical movement from roots to leaves and vice versa. The assembled vegetation model was integrated in an existing dynamic air/soil model (SoilPlus) described in detail in *Ghirardello et al., 2010*. **Figure 1** shows a schematic representation of the vegetation compartments and their relationships with the air and the litter/soil compartments of the SoilPlus model. The resulting model (SoilPlusVeg) includes: 1) two air compartments, namely lower air (LA) and upper air (UA) representing the PBL and the residual layer respectively, which

vary in height and wind speed on an hourly basis; 2) a multi-layered soil, bare or covered by up to three litter horizons; 3) a vegetation compartment which can be composed of a mono-specific or a multi-specific forest but it can also be parameterized to reflect the characteristics of herbaceous plants and pasture systems. When the vegetation model was integrated in SoilPlus, it was assumed that the new compartments (roots, stem, and leaves) did not change the volume of the other ones (UA, LA, litter and mineral soil) and that vegetation evapotranspiration, although calculated by the model, it was not parameterized at species level. Furthermore, in order to distribute root volume in each soil layer, considering the rooting distribution in soil, the Gale and Grigal model (*Gale and Grigal, 1987)* was chosen (more details are given in **Appendix A.6).** The litter/soil organic matter (OM) mass balance of the SoilPlus model was improved considering OM deriving from falling leaves (**Appendix A.13**). Moreover, mass transfer coefficients (MTC) and D values for the air-soil exchanges were modified in order to consider the influence of the vegetation presence. More specifically, MTC for absorption (K_{EV}) and dry particle deposition (U_Q) to soil were modified during the vegetation period to consider the reduced turbulence of air under the plants; in addition, D values for rain dissolution ($D_{RDissLA}$) and wet particle deposition (D_{WDepLA}) were modified considering the fraction of water that drip to soil after/without intercepting leaves, while D value for dry particle deposition D_{DDepLA} was correct to consider the particles not intercepted by leaves (**Appendix A.12**). In the model presented here, each compartment is described by a time dependent mass-balance equation written in differential form in which the chemical amount (mol) is the state variable. The left-hand terms of the equations represent the variation of the chemical amount (mol) in the compartments with time (**Table A.10**). The letters **a- φ** include the terms involved in the mass balance (**Table A.11**). The mass balance equations are 1st-order ordinary differential equations (ODEs), and the system is solved numerically using a 5th-order accurate, diagonally implicit Runge-Kutta method with adaptive time stepping (ESDIRK) *(Semplice et al., 2012)*. More details about model parameterization can be found in the Supporting Information (**Appendix A.1-A.14)**.

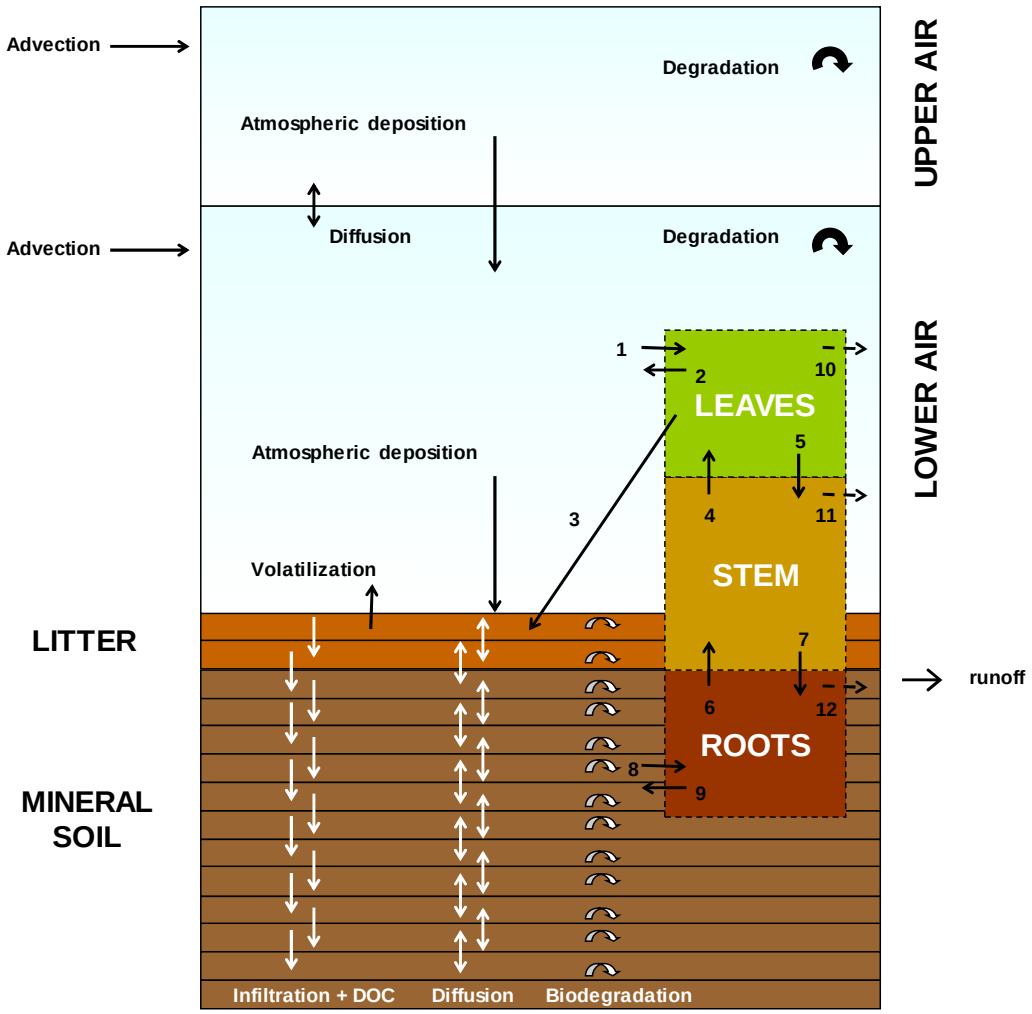

Figure 1 - Schematic representation of SoilPlusVeg model. The numbers indicate the vegetation compartment processes: 1) Air-leaf transfer (absorption + dry particle deposition + wet particle deposition + rain dissolution); 2) Volatilization; 3) Leaf-soil transfer (wash-off + wax erosion + litterfall); 4) Stem-leaf transfer; 5) Leaf-stem transfer; 6) Roots-stem transfer; 7) Stem-roots transfer; 8) Soil-roots transfer; 9) Root-soil transfer; 10) Degradation in leaves; 11) Degradation in stem; 12) Degradation in roots. DOC stands for Dissolved Organic Carbon.

2.2 Sensitivity analysis. A preliminary sensitivity analysis was conducted for phenanthrene (PHE) and pyrene (PYR) as reported in **Appendix B.1** according to *MacLeod et al., 2002*, to investigate which input parameters (I) have the strongest influence on three outputs (O), i.e. concentrations in LA, leaves and litter. The sensitivity (S) for the selected output parameters (O) to changes in the individual parameters (I) was evaluated by varying each input individually by 0.1% and by assessing the absolute sensitivity of the outputs to these changes as follows:

$$|S| = \left| \frac{\Delta O / O}{\Delta I / I} \right| \qquad \textbf{Eq.1}$$

where ΔO and ΔI are the relative changes in the output and the input parameter, respectively.

Three output parameters (PHE and PYR concentrations in LA, leaves and litter) and 50 input parameters were selected for the sensitivity analysis. More specifically, concentrations of the last hour of a year simulation were considered.

2.3 Simulation scenario for the model evaluation. An evaluation of the SoilPlusVeg model performance was carried out for two Polycyclic Aromatic Hydrocarbons (PAHs), PHE and PYR (**Table B.1**) comparing model output of a one-year simulation with a dataset of leaf concentrations measured in a small broadleaf woods located in Northern Italy (Como) in 2007 *(Terzaghi et al., 2015).* The vegetation compartments were parameterized as reported in **Appendix A**. Simulations were performed for a mixed broadleaf woods, composed of *Cornus mas* (cornel), *Corylus avellana* (hazelnut) and *Acer pseudoplatanus* (sycamore maple). Bud burst occurred on 15 March 2012 for the two understorey species (cornel and hazelnut), while maple leaves appeared about 3 weeks later, on 7 April. The growing season ended on 5 December but comparison between predicted and measured results was performed for a shorter period (15 March -7 June) and for only two species (cornel and maple). The air compartments were parameterized as reported in *Morselli et al., 2011*. Upper air height ranged between 10 m to 2267 m while that of lower air between 100 m and 3000 m, depending on the season and the period of the day (day or night). Wind speed in upper air ranged between 0.2 m/s and 43 m/s, while in lower air between 0.2 m/s and 33 m/s. Such data were calculated with the help of a meteorological pre-processor (for details, see *Morselli et al., 2012*) starting from upper air soundings and standard meteorological observations collected during 2007 for a semi-urban site located in the proximity of Milan, about 50-km away from Como. Even though the topographical setting of Como (situated North of Milan, bordering to the Alps mountains) could determine differences in PBL height and dynamics with respect to the Milan site (substantially flat), this meteorological dataset was used

because of its completeness and given the lack of an upper air sounding station in the surroundings of Como. A single litter horizon (Oi) characterized by dynamic depth (~0.5 cm to ~3.5 cm), high porosity, low field capacity and wilting point (see **Appendix C.1** for more details) and a 10 cm deep loamy sand soil were simulated. The total thickness of the litter/soil system was ~10.5 cm - ~13.5 cm depending on the period of the year. While the soil horizon was subdivided into a number (20) of 0.005-m thick layers, a single layer of dynamic depth was considered for the litter horizon to evaluate how the change in some properties (such as porosity and organic carbon) would influence the fate of chemicals in this compartment. Organic carbon (OC) fractions were set to 56% and 4% in the litter and soil compartments respectively, while averaged DOC concentrations of 10 mg/L (mineral soil) and 20 mg/L (litter) were assumed in spring, multiplied by a factor of 3 and 2 in summer and fall respectively, and a factor of 0.5 in winter to obtain an annual average concentration of ~15 mg/L (mineral soil) and ~30 mg/L (litter) (*Michalzik et al., 2001*). These assumptions were made to reconstruct a seasonal DOC production profile as described in the literature (*Kalbitz et al., 2000*). The Oi horizon was assumed to be composed of fast degrading leaves, with an average half-life of 84 days (*Jacob et al., 2009*); the mineral soil had instead more persistent organic carbon (1% reduction in a year of simulation) to simulate typical humified organic matter. Meteorological parameters such as temperature, precipitation, solar radiation and PM_{10} concentrations were provided by the Regional Environmental Protection Agency *(ARPA, 2014)* on an hourly or daily basis for 2007 for Como city. In order to run the model, an estimate of the emission conditions was needed. The PAH sources were calibrated to reflect the observed range of variability in measured concentrations (*Terzaghi et al., 2015).* More specifically, the direct chemical and PM_{10} emission to lower air were calibrated in order to obtain the best possible fit to the range of measured air concentrations (average of the week), while a PM_{10} background concentration equal to the lowest measured concentration (7 $\mu g/m^3$) was assumed. No background concentration for chemical was considered. In **Appendix C.2** more details about chemical emission in LA can be found.

2.4 Simulation scenario for the model illustration. The following illustrative simulations (i, ii, iii) were performed**.** i) The short-term variability of PHE air-leaf exchange was investigated. More specifically air-leaf fluxes obtained from model evaluation simulations were interpreted considering the daily variability of meteorological parameters, air compartment structure and chemical emission. ii) Five PCBs of different physical and chemical properties (**Table D.1**) were simulated to investigate the seasonal variability of chemical fluxes in a forested system mainly focusing on air-leaf-litter exchange. A one year simulation was run adopting the same scenario described in section 2.3, but assuming a chemical background concentration of ~13, 10, 5, 3, 2, 1 pg/m^3 for PCB 28, 52, 101, 153, 180 respectively and a PM_{10} background concentration of 15 µg/m^3, which are in the range of concentration measured by our group in a remote forested area (Lys Valley) located in Northern Italy (*Nizzetto et al., 2008b*). iii) The role of a contaminated litter/soil system in acting as a possible PCB source for the overlaying vegetation was estimated with another one year simulation, maintaining the background air concentration to zero and setting the same chemical amount reached in litter and soil at the end of previous simulations.

RESULTS AND DISCUSSION

3.1 Sensitivity analysis. The sensitivity of the three outputs to changes in the most influential input parameters are shown in **Figure B.1-Figure B.3**, while a complete list of results can be found in **Table B.2.** PHE and PYR concentrations in LA were mostly affected by emission in LA (*MOL_LA*), LA height (*HeightLA*), wind speed in LA (*WindSpeedLA*) (*S*~1) and domain size (*SimArea*) (S~0.5). These parameters affected similarly concentrations in leaves and litter. For PHE and PYR concentration in leaves one of the most influential parameters was air temperature (*HourlyTemp*) (S~1.5), followed by plant-air partition coefficient (*Kpa_monosp*) (*S*~0.7 and *S*~0.5 for PHE and PYR respectively) and other parameters involved in the K_{PA} estimation (Specific Leaf Area (*SLA*) (S~1), enthalpy of phase change between plant and air (*DeltaHPA*) (S~0.8) and SLA at full development of leaves (*SLAstable*) (*S*~0.7 and *S*~0.5 respectively)). Considering litter concentration, organic carbon

partition coefficient (*Koc*) (S~1) was among the most sensitive parameters followed by some physical and chemical properties (water solubility (*WS*) (S~0.8 and S~0.6, respectively) and vapour pressure (*VP*) (S~0.8 and S~0.6, respectively)) and air temperature (*HourlyTemp*) (S~0.6 and S~1, respectively). In addition, DOC partition coefficient (*Kdoc*) and DOC concentration (*DOCconc*) seemed to affect litter concentrations, although with a different degree for the two chemicals (S~0.2 and S~0.7, respectively). Being a local sensitivity analysis (i.e., one parameter varied a little at a time), the approach presented here did not allow capturing, for example, the effect of the interactions among parameters *(Augusiak et al., 2014)*; however, it helped in the identification of the key input parameters to which particular attention should be paid in order to obtain accurate results.

3.2 Model evaluation

3.2.1 Predicted vs. measured leaf concentrations. Hourly predicted concentrations in cornel and maple leaves were compared with data measured over a three-month period (15 March – 7 June) reported in *Terzaghi et al., 2015* (**Figure 2**). More specifically, measured concentrations were compared with values predicted at h 12:00 of each sampling day to match leaf time collection (between h 11:00 and h 13:00). Modelled concentrations in leaves (solid lines) generally reproduce the seasonal pattern of the measured ones (black dots), in which leaf concentrations oscillate within a small range according to the air concentration trends influenced by chemical emission and meteorological parameters (*Terzaghi et al., 2015*). Only cornel leaves, which appeared 3 weeks before maple, show a concentration reduction after the first sampling event (29 Mar), caused by a decrease in air concentrations. **Figure C.11** shows the comparison between: 1) measured, 2) predicted at h 12:00, and 3) predicted daily average concentrations for each sampling day. Model results showed a good agreement with measured data, considering both plant species and both chemicals, with a quotient between predicted and measured concentration (**Figure C.1**2) that ranged between 0.5 to 2.5 (PHE, maple), 0.4 to 1.3 (PHE, cornel), 0.4 to 2.4 (PYR, maple) and 0.6 to 2.3 (PYR, cornel). The accuracy of SoilPlusVeg model predictions was similar to that of other dynamic bioaccumulation

models which include a vegetation compartment (*Ftanke et al., 2011; Nizzetto and Perlinger, 2012; St-Amand et al., 2009; Undeman et al., 2009*). Some 10-year long simulations were previously performed to verify the possible role of increasingly contaminated litter and mineral soil to influence the air compartment; this resulted in a volatilization flux from litter which represented just <0.05% of direct emission in air and caused variations in air and leaf concentrations lower than 0.01% and 0.8% respectively, therefore not deviating from measured concentration significantly.

3.2.2 Importance of spatial/temporal specific scenarios. Box-plots in **Figure C.13** show the daily variability of predicted concentrations: measured values (black bars) generally fall between the 10^{th} and 90^{th} percentile of the daily predicted concentration distribution or were close to the minimum or the maximum with a few exceptions. Predicted concentrations in leaves varied by a factor of 1.4 to 5.4 for PHE and 1.1 to 1.4 for PYR within the day (considering min and max values) due to the influence of meteorological parameters and air compartment structure. However, given the rapid response of leaves to air temperatures (Terzaghi et al., 2015) the sometimes observed discrepancy between measured and predicted concentrations in leaves could also be ascribed to a difference of air (and therefore leaf) temperatures between prediction and sampling time. Additionally, the sometimes measured concentrations are closer to predicted concentrations at a different time than h 12:00. This could be ascribed to the scenario adopted to run simulations and other uncertainties in model parameterization. The model scenario employs meteorological and ecological parameters and air compartment structure which were not measured exactly at the same time (SLA, LAI) or place (PBL height, wind speed, rainfall, solar radiation, temperature) of leaf concentrations. Furthermore, due to lack of information, chemical emission was calibrated considering weekly average air concentration and traffic as possible source of PAHs, ignoring the possibility of higher peak emissions on specific days of the modelled period. Some of these parameters (temperature, emission to air, lower air height, wind speed and SLA) resulted to significantly influence (S ~1) leaf concentration during the sensitivity analysis. Recently *Takaki et al., 2014 and Trapp, 2015* have recognized the importance of using site-specific data to improve the accuracy of predictions when modelling organic compound

accumulation in vegetation. This could explain PHE and PYR prediction for maple leaves on 12 April for example: the overestimation by a factor of ~2 could be ascribed to the maple SLA value which being at its maximum level influenced accumulation increasing K_{PA} (see **Eq. (A.14)**). More specifically, ecological parameters used to build the evaluation scenario were measured in 2012, five years later than the PAH determination in air and leaves; although the beginning of the 2012 growing season was shifted to match the leaf development start of 2007 (*Terzaghi et al., 2015*), the time employed to reach maximum SLA value after bud burst during the different vegetative seasons was assumed not to change, although a delay of about 1 week was observed (data not shown) during two consecutive vegetation seasons (2011 and 2012) in the same woods. Predicted concentrations in the two species did not always show the same deviation from measured values; this probably depends on: 1) species-specific features that now in SoilPlusVeg are assumed to be the same for both species such as permeance into the cuticle and mass transfer coefficient for absorption and dry particle deposition; 2) not species-specific air-leaf chemical fluxes but referred to canopy as a whole, SoilPlusVeg being a "big leaf" model and 3) the emission calibrated to match measured air concentration (at 1.5 m height) probably better represented cornel exposure conditions (being an under canopy species) rather than those of maple (upper canopy species). However, given the conditions outlined above, the predicted results are considered to give consistent and satisfying results, confirming the adequacy of the simulation scenario and parameters applied.

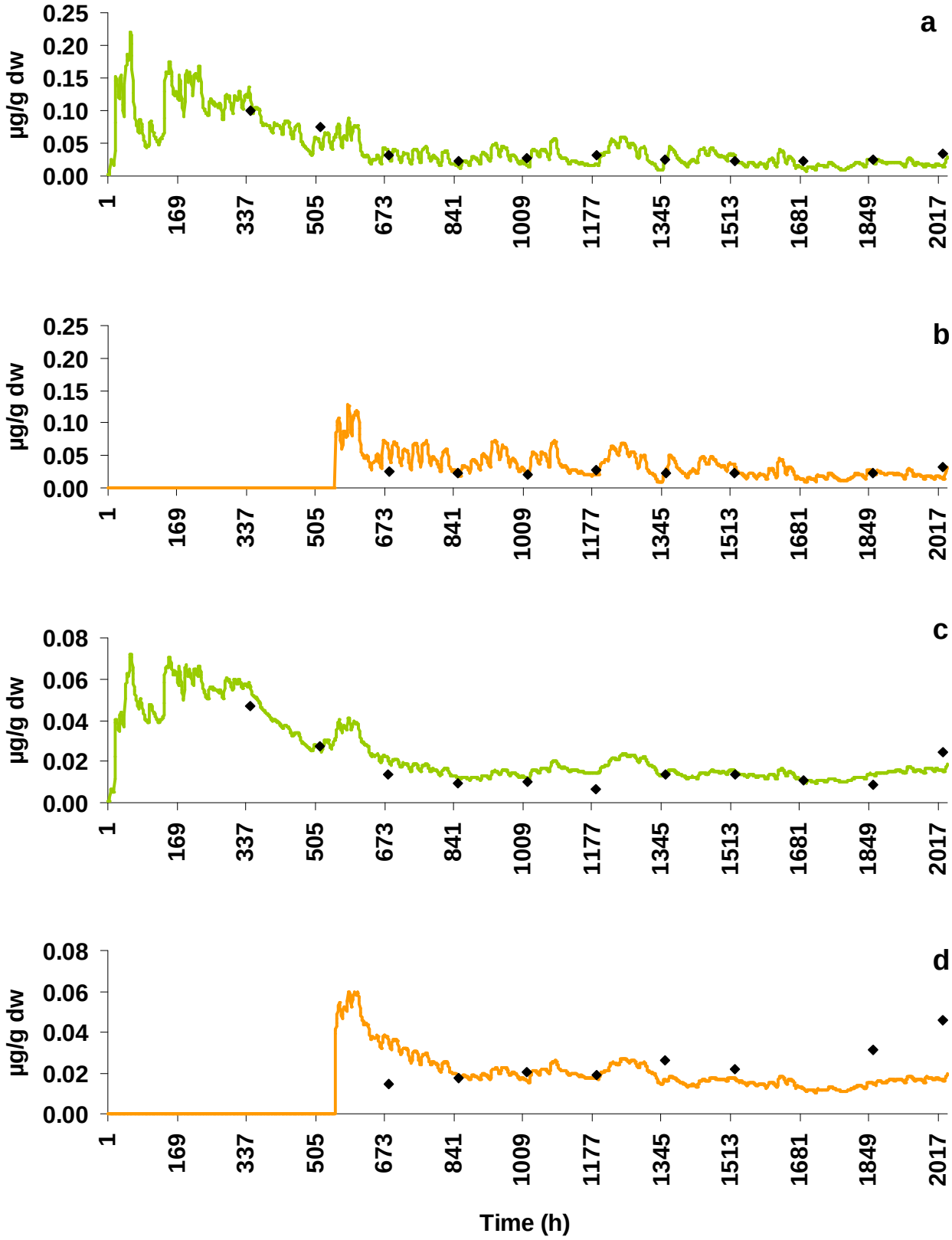

Figure 2- Comparison between PHE (a and b) and PYR (c and d) predicted (solid line) and measured (black dots) concentrations (µg/g dw) in leaves of cornel (green, a and c) and maple (orange, b and d)

3.3 Model illustration

3.3.1 Short term variability of air-leaf exchange (i). The diurnal variability of air-leaf exchange was investigated considering the fluxes resulting from model evaluation. This is important to evaluate potential reversal of flux during the 24h cycle and its significance. **Table D.2** summarizes yearly min, max, mean and median input and output fluxes to/from leaves for PHE and PYR. Again, fluxes refer to the canopy as a whole and not to single species. Absorption followed by volatilization and degradation were the most important fluxes to and from leaves. A three-day period (11-13 April) was chosen to evaluate how the variability of meteorological parameters, together with chemical emission in air, can influence the uptake/release of PAHs by plants. PHE air and leaf concentrations, PBL height and chemical emission trends during the selected period are depicted in **Figure D.1**, while absorption and volatilization fluxes to/from leaves are reported in **Figure 3** together with PBL height and temperature.

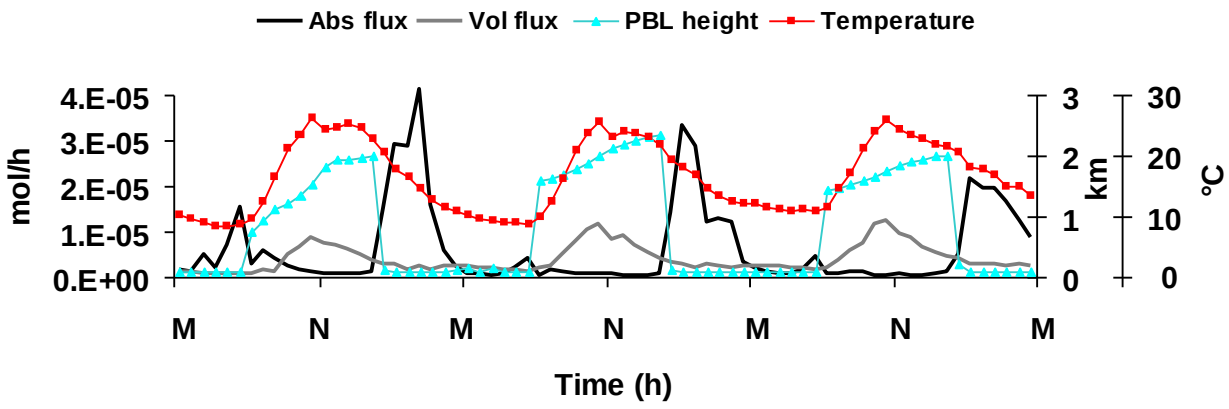

Figure 3 – Absorption, (solid black line) and volatilization (solid grey line) fluxes (Abs flux and Vol flux respectively), temperature (red line with square marker) and PBL height (light blue line with triangles marker) trend during a three-day period (11-13 April) for PHE. "M" means midnight while "N" stands for noon.

Predicted concentrations in leaves followed air concentration changes caused by the variability of PBL height and chemical emission. In general air concentrations were higher during night time hours when PBL was low and chemical emission was still high (e.g. from 18 to 22 h of 11 April). On the contrary, during night time hours characterized by lower emission (e.g. from 1 to 5 h of 12 April), PBL influence was less evident. During daytime hours, despite the higher chemical emission, the

increase of PBL height caused a dilution of chemical in air resulting in lower concentrations. Generally, night time air concentrations exceeded day time concentration of an average factor of 16 in this 3-day period. As appears from **Figure 3** and **Table D.3,** during certain hours the volatilization flux of PHE from leaves exceeded absorption indicating that leaves could act as "dispensers" of air contaminants, not just air "filters", depending on meteorological conditions. More specifically, chemical release from leaves could happen both during daytime hours (driven by temperature mediated volatilization together with chemical gradient inversion caused by the increase of PBL height) and during part of the night time hours (caused by emission reduction and therefore chemical gradient inversion). Concentrations in leaves were a factor of ~2 higher at evening (after 5 p.m.), night and early morning (until 7/8 a.m.) hours with respect to the other period of the day. This is an example of typical behaviour and it agrees with *Hung et al., 2001* which showed that the diurnal variation in grass concentration caused by the temperature-induced exchange of PCBs between the plant surface and the atmosphere resulted in highest concentrations at 6 am (45 pg/g) and the lower concentration throughout the warmer parts of the day (20-30 pg/g). Therefore, plant leaves can be seen as a dynamic compartment which contributes to the diurnal variation of organic contaminant air concentrations, which deposit or volatilize from their surface in response to changes in environmental conditions *(Hornbuckle and Eisenreich, 1996; Gouin et al., 2002; Nizzetto and Perlinger, 2012; Bao et al., 2016)*. Leaves can be one of the major air short-term sources and sinks of many persistent organic compounds (*Dalla Valle et al., 2004),* considering their surface area.

3.3.2 Seasonal variability of air-leaf-litter exchanges (ii). Preliminary comparisons showed good agreement (within a factor of 1.2-3.9) between predicted and measured concentrations in leaves and litter collected in the Lys Valley (Nizzetto *et al., 2008b; Moeckel et al., 2008*) indicating that, with a more detailed and site-specific scenario definition, SoilPlusVeg would be a powerful tool to predict and understand chemical fate in vegetated systems. Predicted concentrations in mineral soil were orders of magnitude lower than the measured ones, with the measured values being the result of more

than 70 years of exposure, depending on PCB production and use (Kimbrough and Jansen, 1989). **Figure D.2** shows air, leaf, litter and mineral soil (average of 10 layers) fingerprints at the end of the year: in the air compartment the less chlorinated compound (PCB 28) predominated, while in leaves and Oi layer a higher contribution of more chlorinated PCB appeared; moving from litter to soil, less hydrophobic congeners dominated the fingerprint (**Figure D.3**). This can be attributed to diffusion and leaching of more water soluble congeners in the dissolved phase. The transport of freely dissolved chemicals masked DOC mediated infiltration, which should favor the more hydrophobic chemical movement (*Moeckel et al., 2008*). This behaviour is shown in **Figure D.4**, where diffusion, leaching fluxes of truly dissolved and DOC associated PCB 28 and PCB 180 are depicted. In order to investigate the seasonal variability of chemical fate and cycling in the air-leaf-litter system, the least and the most hydrophobic congeners (PCB 28 and PCB 180) were selected for comparison. Note that, although included in the mass balance, air-leaf exchange was not shown here, being investigated in detail in the previous section. **Figure 4** shows the seasonal accumulation (ng/m^2) for a clean litter compartment exposed to background contaminated air for a one-year simulation. A different picture appeared for the two compounds of contrasting physical and chemical properties: while PCB 180 accumulated during the whole year being less affected by loss processes, PCB 28 accumulation occurred for a shorter period (the first month) when the constant chemical input from air (leaves had not appeared yet) was not exceeded by chemical losses. In the following months, litter exhibited a reduction in PCB 28; about 70% and 30% of the input fluxes were re-volatilized in air or transferred to mineral soil (diffusion + infiltration) respectively; at the end of the year, litter fall contributed (mainly in October and November), resulting in a rapid increase.

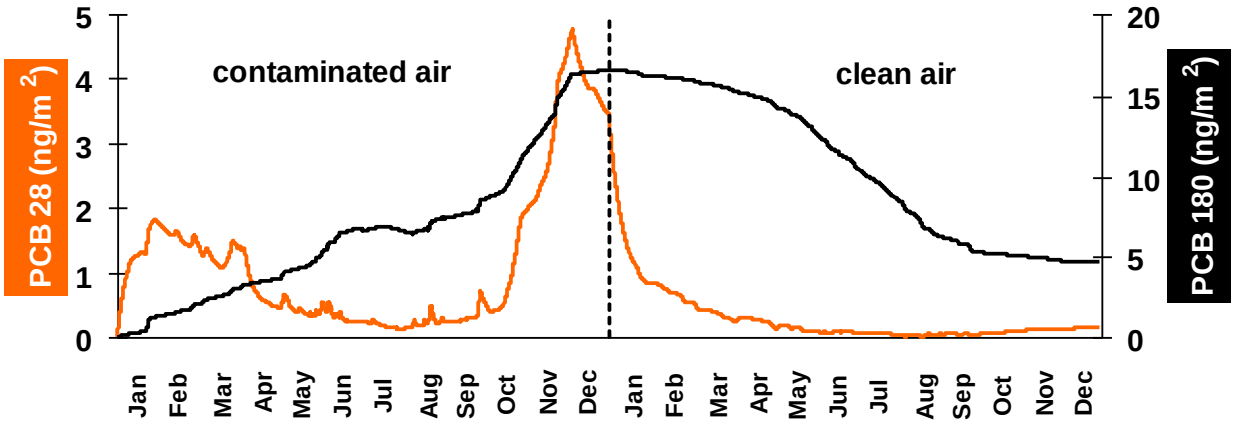

Figure 4 – PCB 28 (orange) and PCB 180 (black) accumulation in litter from background air and reduction following a decline in emissions to air

In **Figure 5** and **Figure D.5,** the seasonal variability of air-litter, leaf-litter, litter-air and litter-mineral soil transfer is compared. PCB 28 air-litter transfer did not show much change during the year with absorption the most important deposition process (~ 95% of annual air inputs). In contrast for PCB 180 wet particle deposition (~ 50% of annual air inputs) contribution appeared during the rainiest months. For both chemicals, leaf-litter exchange assumed higher values during October-November, with litter fall the main process compared to wash-off and wax erosion (90% and 70% of annual leaf inputs for PCB 28 and PCB 180 respectively). PCB 28 negative net fluxes indicated net release from litter towards the air and underlying soil. Re-volatilization was the dominating loss process for PCB 28 representing 30-92% of inputs (air-litter + leaf-litter fluxes), with the maximum during the hottest month (July) **Figure D.6**, while it was lower for PCB 180 (0.10-25%). Transfer to deeper layers mainly occurred through diffusion for PCB 28 (10-58% of inputs) and both by infiltration and diffusion for PCB 180 (0.75-41% and 0.14-56% respectively). In particular conditions, when the infiltrating water was maximized (heavy rainfall) and DOC concentrations were higher (i.e. August, September, and November), the role of DOC accounted for 55-87% of PCB180 losses, compared to 3-15% from volatilization and 5-23% from diffusion. Biodegradation was negligible for both chemicals (<2% of inputs). This is in agreement with *Liu et al., 2013* who reported that, litter volatilization fluxes represented about 70% and 30% of total loss for PCB 28 and PCB 180 (native

congeners) respectively and that leaching fluxes tended to be higher than volatilization for heavier compounds. However, when a contaminated soil is considered (such as in Lys Valley, with PCB 28 and PCB 180 at 62 and 430 pg/g d.w. respectively) the fluxes do change in direction and amount: for PCB 28 volatilization goes up to a factor of 20 (with a maximum of about 1200 µg/month) and diffusion direction is now upwards; for PCB 180 volatilization goes up of a factor of 5 (with a maximum of about 10 µg/month) and here as well the diffusion direction is upwards.

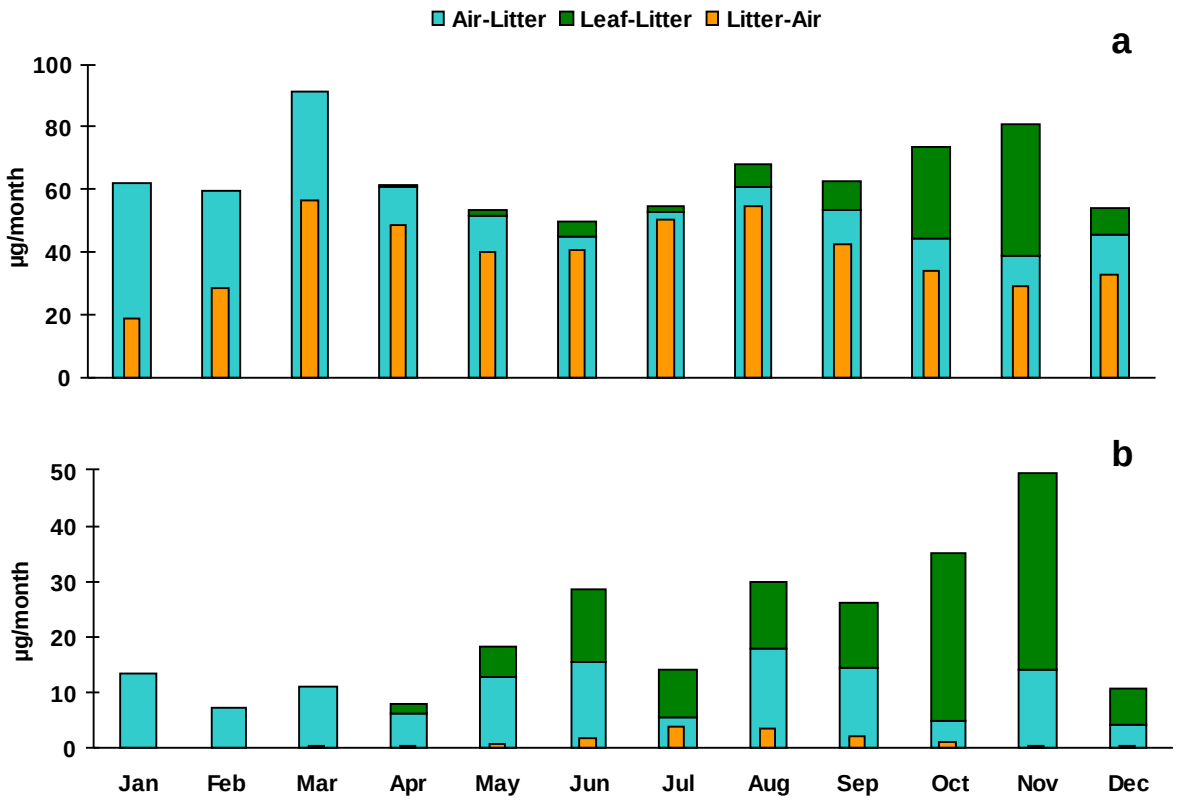

Figure 5- Air-litter (light blue), leaf-litter (green) and litter-air (orange) fluxes (µg/month) of PCB 28 (a) and PCB 180 (b)

The results presented here show that the seasonality driven by air temperature (which influences re-volatilization), rainfall and DOC concentrations (which influence infiltration) appeared to be relevant in determining PCB concentrations in litter and their mobilization towards the adjacent compartments. Some litter characteristics, i.e. OM content and total porosity, may also play an important role in influencing litter concentrations. For PCB 28, remobilization of substantial amount stored previously was favoured by OM mass mineralization before litter fall starts: because of its

physical chemical properties (lower K_{OC}) PCB 28 can reach equilibrium between air and mineral soil faster than PCB 180; OM decomposition increased PCB 28 fugacity resulting in a fugacity gradient back to overlying air and to underlying soil (*Moeckel et al., 2008*). Litter porosity instead, is involved in volatilization and diffusion processes; the simulated litter was characterized by a high porosity (0.95-0.99 cm^3/cm^3) and a low bulk density (0.002-0.015 g/cm^3), being made up of dead leaves not yet formed into a compact layer. This would enhance chemical movement from litter towards air and mineral soil through volatilization and diffusion. Compared to a mineral soil layer (total porosity of 0.44 cm^3/cm^3), the volatilization and diffusion potential could be double for this type of litter. Total porosity could vary moving from organic horizons to mineral layers, but also from broadleaf to conifer species: broadleaf litter has a large surface area and often "curls" create air spaces within the litter layer (**Figure D.7**); this gives less mass per volume than a needled litter layer produced in a pine forest (*Ottmar and Andreu, 2007*). Moreover, broadleaf litter is typically fresher and less compact in late summer/autumn than in winter/spring when snow or rainfall events can compress it. This highlights the need to measure litter porosity and composition evolution to obtain accurate prediction of chemical fluxes for different type of forests. Recently, OM turnover (*Zheng et al., 2015*) and forest species composition (broadleaves vs. conifers) (*Komprdová et al., 2016*) were identified to be key factors in influencing organic chemical fate in the litter/soil system; organic chemical translocation from upper to lower organic horizons appeared to be more rapid in the broadleaf deciduous forest due to faster litter and OM turnover compared to mixed and coniferous forests.

3.3.3 Potential of a contaminated soil-litter system to recharge the atmosphere (iii). PCB 28 showed a more dynamic behaviour in response to air chemical emission cease, since in 85 days 90% of the amount accumulated in the previous year was lost, with about the 80% lost in the first month (**Figure 4)**; this compared to a reduction of just 6% for PCB 180 (**Figure D.8**). PCB 28 left the litter compartment mainly by volatilization and diffusion to depth (~35% and 60% of output respectively); in contrast infiltration was the main loss process for PCB 180 (24-86%), followed by diffusion to depth (6-49%). Diffusion to depth was also important for PCB 28, but balanced by diffusion up, did

not cause net losses. The role of litter as a potential source for air and therefore vegetation is represented in **Figure D.9**, where the response of air concentration related to PCB 28 and PCB 180 transfer from litter is shown. Litter, similarly to what was shown for the leaves, seems to act as a source for air and therefore vegetation, in particular situations, for example, when air concentrations decreases due to a change in wind direction bringing less contaminated air.

3.4 Relevance for risk assessment

The knowledge of the dynamics of air/plant/litter/soil interaction may be useful when evaluating the exposure of humans and ecosystems in many ways. For example, diel variation of concentrations in air could be deeply influenced by the presence of vegetation and litter, as well as by the seasonality and meteorological conditions. Similarly, vegetation concentrations of toxic chemical can vary in time, possibly showing unexpected behaviours: after an initial phase of accumulation, concentration in leaves can respond dynamically to air concentration changes and therefore if vegetation biomass is used as food by humans or other consumers in the ecosystem (e.g. cattle) could determine a variable exposure depending on time, season, species and meteorological condition when grazing or consuming.

4. Conclusions

A new dynamic vegetation model (SoilPlusVeg) that accounts for the variability of meteorological and ecological parameters was developed and integrated in an existing dynamic air/litter/soil model. A preliminary sensitivity analysis highlighted the importance of the air compartment structure, meteorological/ecological variability, litter characteristics and chemical emission in influencing air, leaf and litter concentrations. During the model evaluation procedure, good agreement between measured and predicted leaf concentrations was obtained. The importance of using site-specific data to parameterize the model in order to improve the accuracy of model predictions was recognized. Three model illustrations revealed the “dual behaviour” of leaf and litter compartments. Both leaves

and litter behaved as dynamic compartments which could accumulate or reemit organic chemicals. The SoilPlusVeg model could therefore be considered a powerful tool to understand and estimate chemical fate and recycling in forested systems, in the evaluation of the exposure of humans and ecosystems to organic chemicals.

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6. Appendix A-D. Supplementary data.

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